## Exhibit 14.05

United States' Motion to Enter Consent Decree, United States v. Alden Leeds, Inc. et al., Civil Action No. 22-7326 (D.N.J.)

# **EXHIBIT A-25**

**Appendix A to** OxyChem's Comments in Opposition to Proposed Consent Decree, *United States v. Alden Leeds, Inc., et al.*, Civil Action No. 2:22-cv-07326 (D.N.J.)

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### Inadvertent Polychlorinated Biphenyls in Commercial Paint Pigments<sup>†</sup>

DINGFEI HU AND KERI C. HORNBUCKLE\* Department of Civil & Environmental Engineering and IIHR-Hydroscience and Engineering, The University of Iowa, Iowa City, Iowa 52242

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A polychlorinated biphenyl (PCB) that was not produced as part of the Aroclor mixtures banned in the 1980s was recently reported in air samples collected in Chicago, Philadelphia, the Arctic, and several sites around the Great Lakes. In Chicago, the congener 3,3'-dichlorobiphenyl or PCB11 was found to be the fifth most concentrated congener and ubiquitous throughout the city. The congener exhibited strong seasonal concentration trends that suggest volatilization of this compound from common outdoor surfaces. Due to these findings and also the compound's presence in waters that received waste from paint manufacturing facilities, we hypothesized that PCB11 may be present in current commercial paint. In this study we measured PCBs in paint sold on the current retail market. We tested 33 commercial paint pigments purchased from three local paint stores. The pigment samples were analyzed for all 209 PCB congeners using gas chromatography with tandem mass spectrometry (GC-MS/MS). More than 50 PCB congeners including several dioxin-like PCBs were detected, and the PCB profiles varied due to different types of pigments and different manufacturing processes. PCB congeners were detected in azo and phthalocyanine pigments which are commonly used in paint but also in inks, textiles, paper, cosmetics, leather, plastics, food and other materials. Our findings suggest several possible mechanisms for the inadvertent production of specific PCB congeners during the manufacturing of paint pigments.

#### Introduction

Polychlorinated biphenyls (PCBs) are a family of 209 compounds, called congeners, produced commercially as Aroclors by chlorination of biphenyl. The Aroclor mixtures were marketed for use in electrical transformers, capacitors, heat transfer systems, and hydraulic systems (1, 2). Lower quantities were used in voltage regulators, adhesives, caulking compounds, inks, lubricants, paints, sealants, carbonless copy paper, coatings, electrical switches, plasticizers, circuit breakers, dust control agents, and older fluorescent lighting fixtures (2). Aroclors were used in paint formulations as drying oils (resins) and plasticizer or softening agents (liquids). Data provided to EPA indicate that PCBs have been found in dried paint at concentrations that range from less than 1 ppm to 97,000 ppm (3).

Some PCB congeners, usually called non-Aroclor PCBs, are not present or are very low in concentration due to unfavored or improbable formation during the Aroclor manufacturing process (2). PCB11 is one of such non-Aroclor PCB congeners. In air samples from Chicago collected in 2007, we found PCB11 widely distributed throughout the city (4). The compound was almost simultaneously reported in air of polar regions (5). Since then, its presence was also reported in air of Philadelphia (6) and five sites around the Great Lakes (7). It appears that PCB11 is a global pollutant. In addition, PCB11 was measured in the wastewater effluent from paint production. Possible production of PCB11 from dechlorination is not likely because its possible precursors are in very low concentration in Aroclors (8, 9). The widespread distribution of PCB11 throughout Chicago and elsewhere suggests volatilization of this compound from surfaces. Litten et al. reported that PCB11 was in surface waters and effluent waste streams from a pigment manufacturing plant around New York Harbor (10). Recently, Rodenburg et al. detected it in consumer goods including newspapers, magazines, and cardboard boxes, which usually contain color pigments (11). Therefore, we hypothesize that PCB11 and other PCB congeners are present as byproduct in current commercial pigments.

Paint is composed of pigments, solvents, resins, and various additives (12). Two major groups of paints are latex (water-based) and alkyd (oil-based) paints (13). The major difference between latex and alkyd paints is that the major liquid portion of latex paints is water while the liquid in oil-based paints consists of petroleum distillates and other organic solvents such as toluene and xylene. Latex paints are the most common type for house use from exterior paint and trim, to interior walls and woodwork. Generally, a paint store has about 10 different colors of base pigments, and paints are sold by mixing pigments with other components. To test our hypothesis, we purchased and analyzed paint pigments from three paint stores. According to IBISWorld Inc., in 2007 these companies account for about 70% of the market share in the United States.

#### **Materials and Methods**

**Reagents.** Paint pigments were purchased from three different paint retailers: Sherwin Williams, PPG Pittsburgh, and Vogel, in Iowa City, Iowa in 2009. A calibration standard solution with a full suite of 209 PCB congeners was prepared from five PCB congener solutions purchased from AccuStandard (New Haven, CT). Acetone and hexane (pesticide grade) were purchased from Fisher Scientific (Fair Lawn, NJ).

Sample Analysis. The extraction method was modified from U.S. EPA method 3545 (14). In brief, approximately 5.0 g of the fresh pigment sample was accurately weighed and mixed with combusted diatomaceous earth, then spiked with 50 μL of 500 ng/mL surrogate standards containing PCB14 (3,5-dichlorobiphenyl), PCB65 (2,3,5,6-tetrachlorobiphenyl) and PCB166 (2,3,4,4',5,6-hexachlorobiphenyl) (Cambridge Isotope Laboratories, Inc.). The samples were extracted utilizing a pressurized fluid extraction (Accelerated Solvent Extractor, Dionex ASE-300) with a mixture of acetone and hexane (1:1, v/v). The extract was concentrated to  $\sim 2$  mL from ~200 mL, and the concentrated extract was transferred to a glass test tube; ~2 mL of concentrated sulfuric acid was slowly added and mixed. Hexane (8 mL) was used to extract the acidified mixture 3 times after a 10-min mechanical shaking and centrifugation at 3000 rpm/min for 5 min. The pooled extract was concentrated down to ~2 mL and passed

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<sup>\*</sup> Corresponding author phone: (319) 384-0789; fax: (319) 335-5660; e-mail: keri-hornbuckle@uiowa.edu.

through a silica gel column prepared with 0.1 g of combusted silica gel at the bottom and 1 g of acidified silica gel (2:1silica gel:concentrated sulfuric acid by weight). Hexane (10 mL) was used to elute PCBs from the column and the eluate was concentrated down to  $\sim\!0.5$  mL for PCB analysis. All samples were analyzed in duplicate, and the average is reported.

The final extract was spiked with 20 ng of PCB204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl) as internal standard (Cambridge Isotope Laboratories, Inc.). All 209 PCB congeners, in about 170 chromatographic peaks, were analyzed using a gas chromatograph with mass selective detection (GC-MS/MS) modified from the EPA method 1668A (15). The quantification of PCB congeners was performed by an Agilent 6890N gas chromatograph with an Agilent 7683 series autosampler coupled to a Waters Micromass Quattro micro GC mass spectrometer (Milford, MA) operating under electron impact (EI) positive mode at 70 eV and multiple reaction monitoring (MRM), and the trap current was 200  $\mu$ A. The retention windows were defined by PCB parent/ daughter ion pairs from mono- to deca- homologues which were 188/152, 222/152.10, 255.96/186, 291.92/222, 325.88/ 255.90, 359.84/289.90, 393.80/323.90, 427.76/357.80, 461.72/ 391.83, 497.68/427.70, respectively.

**Quality Assurance/Quality Control.** During extraction of paint pigments using ASE, samples and blanks (combusted diatomaceous earth) were alternated on the instrument to avoid, and detect, any cross contamination between pigment samples. The average recoveries of PCB 14, PCB 65, and PCB 166 surrogate standards injected in every sample were  $56\pm15\%$ ,  $85\pm25\%$ , and  $86\pm20\%$ , respectively. Di- to tri- PCB concentrations in samples were corrected for PCB14 recovery and tetra- to deca-PCBs for PCB166 based on our analytical method validation using Standard Reference Material 1944.

#### **Results and Discussion**

Inorganic and Organic Pigments. Inorganic pigments are produced from either naturally mined pigments (sienna, umber, ochre) or synthetically manufactured pigments (iron oxide, carbon black, etc). Titanium dioxide is the most important white pigment in the industry because of its high refractive index, reflectance, ease of dispersion, brightness, and opacity (16, 17). Titanium dioxides and iron oxides account for approximately 70% and 15% of world consumption of inorganic pigments (18, 19). No PCBs were found in inorganic pigments which primarily contain titanium dioxide, iron oxide, raw umber, or carbon black (Figure 1 and Table 1). PCB formation is expected to be associated with chlorinated solvent or intermediates used in the manufacturing process of pigments.

PCBs were primarily found in organic paint pigments with a concentration range from 2 to 200 ng/g fresh weight (f.w.) in 15 of 33 analyzed paint pigments (Figure 1 and Table 1) in this study. Pigment chemical structures were provided by Sherwin Williams. PPG Pittsburgh and Vogel did not provide this information, although we were able to determine several pigment types based on their material safety data sheets. Most orange, red, and yellow pigments are made from azo pigments, and PCBs are only found in two groups of organic pigments: azo pigments and phthalocyanine pigments. For pigment samples from Sherwin Williams, we clearly see PCBs are only present in these two types of pigment. Chlorinated solvents or intermediates are usually involved to produce these two types of organic pigments, and side-reactions of these chlorinated compounds result in formation of PCBs during the manufacturing process. The EPA is aware of the presence of PCBs in diarylide pigments and phthalocyanine pigments. Diarylide pigments belong to the azo category of pigments (20). However, we observed the presence of PCBs not only in diarylide pigments but also in other azo pigments

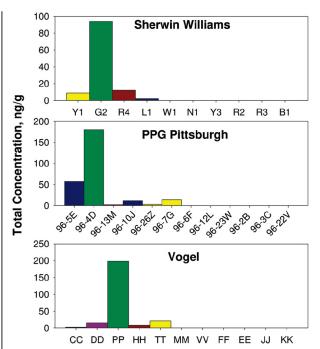


FIGURE 1.  $\Sigma$ PCB concentrations in 33 commercial paint pigments purchased from Sherwin Williams, PPG Pittsburgh, and Vogel paint stores.

such as Hansa yellow, quinacridone, isoindolinone, and maybe more, since some pigment types are unknown.

Azo and phthalocyanine pigments and chemically identical dyes are the most important groups of synthetic colorants with a great variety of industrial applications. They are used for coloring paints, inks, textiles, paper, cosmetics, leather, plastics, food and other materials (21, 29). The widespread use of these pigments explains the presence of PCB11 in commercial goods common throughout modern society, such as newspapers, magazines, and cardboard boxes (11). Although we do not know if inadvertent PCBs have adverse effects on human health, there are many potential routes for human exposure to these PCBs through inhalation, dermal exposure, and ingestion due to their physicochemical characteristics of semivolatility, hydrophobicity, and persistence

**Congener Profiles.** The detailed PCB distribution profile in each pigment is provided in Tables S1-S3, and two examples are presented in Figure 2. The pigments, Y1 of Sherwin Williams and 96-26Z of PPG Pittsburgh, are both yellow and made from monoazo yellow pigments. The synthesis of monoazo yellow pigments involves the coupling of a diazotized substituted aniline with a coupling component containing an active methylene moiety in a linear structure (18). There are different PCB distribution profiles in different pigments due to various manufacturing processes for different pigments or even the same pigments. The same type pigment might have different starting materials, intermediates, or manufacturing conditions. For a particular manufacturing process, only very limited numbers of chlorinated compounds are involved; however, up to 22 congeners were detected in one pigment. Among these detected congeners, PCBs 77, 114, and 123 are dioxin-like congeners which have distinct toxic properties. A variety of PCB profiles in paint pigments were observed in this study (Tables S1-S3), although the reason for their presence is not completely understood. PCB11 was most often detected: it was found in 13 of 15 pigment samples for which any PCBs were detected, followed by PCBs 8, 6, 4, 1, 12/13, 2, 3, and 209—each with more than 40% detection frequency (Figure 2). PCB congeners of all chlorination levels were found in the pigments.

TABLE 1. Colors and Types of Commercial Paint Pigments Purchased from Three Paint Stores<sup>a</sup>

paint store	code	color	pigment type
Sherwin Williams	Y1 G2 R4 L1 W1 N1 Y3 R2 R3 B1	yellow green red blue white raw umber deep gold maroon magenta black	hansa yellow phthalocyanine green isoindolinone phthalocyanine blue titanium dioxide raw umber titanium dioxide iron oxide iron oxide quinacridone carbon black
PPG	96-5E 96-4D 96-13M 96-10J 96-26Z 96-7G 96-6F 96-12 L 96-23W 96-2B 96-3C 96-22 V	blue green durable red carbazole violet medium yellow durable yellow red raw umber white lamp black yellow oxide	phthalocyanine blue phthalocyanine green / / / monoazo yellow / iron oxide / titanium dioxide / iron oxide quinacridone
Vogel	CC DD PP HH TT MM VV FF EE JJ KK	blue magenta green exterior red medium yellow red oxide white raw umber black yellow oxide brown oxide	phthalocyanine blue / phthalocyanine green / / / / / / / / / / / / / / / / / /
"/": proprietary.			

However, lower chlorinated PCB congeners dominated in most pigment samples except in phthalocyanine green pigments which contain very high levels of PCB209 relative to other detected congeners. PCB209 accounts for approximately 66%, 33%, and 50% of total PCBs in phthalocyanine green pigments of G2, 86-4D, and PP, respectively, from three different paint stores. It is interesting that although dissimilar in structure, both PCB 11 and PCB 209 are non-Aroclors that could be used as signatures of pigment use or discharge.

Formation Mechanism. Phthalocyanine Pigments. Copper phthalocyanine pigments are the most widely used blue and green pigments for various applications (16, 21). Two different general processes are used for commercial production of phthalocyanine pigments: one is from phthalic anhydride, urea, and copper or a copper salt, and the second is from phthalonitrile and copper or a copper salt (22). The first route is less expensive and is usually used to produce phthalocyanine pigments for high-volume and low-cost applications such as paint pigments and dyes for textiles and paper; the second route is more expensive but produces high-quality and high-purity phthalocyanine pigments such as charge generation materials for electrophotography (21). The first urea process usually involves organochlorine solvent such as di- or trichlorobenzene as the reaction medium. Uyeta et al. showed that starting materials (urea, phthalic anhydride, copper chloride, ammonium molybdate) and the initial reaction medium (di- or trichlorobenzene) did not contain PCB congeners (22), so they are not a direct source of PCBs in pigments.

PCB formation mechanisms (Figure 3) are proposed for the urea manufacturing process. Phthalocyanine blue is produced from starting materials without chlorines, and phthalocyanine green is derived from phthalocyanine blue by chlorination (21). Lower chlorinated PCB congeners are produced as by-products during the manufacturing process of phthalocyanine blue pigments from the reaction medium chlorobenzene (23). The reaction medium, dichlorobenzene or trichlorobenzene, can form tetra-, penta-, and/or hexa-PCB congeners by a reaction with each other under heat through a free radical mechanism (the dashed arrow pathway in Figure 3) (24, 25). The resulting PCB congeners may thermally degrade further into lower chlorinated congeners by the same mechanism (26). Mono-through tetra-chlorobiphenyls have been created through a free radical mechanism from pyrolysis and combustion of other chlorinated organics at temperatures ranging from 300 to 700 °C (27). The free radical mechanism to form PCBs from chlorobenzenes has been experimentally demonstrated (25). The temperature is usually below 300 °C during the pigment manufacturing process; however, the presence of copper chloride and ammonium molybdate as a catalyst might promote this mechanism at a lower temperature range (25, 28). To gain proper brightness, shade, strength, and flow properties of synthetic pigments, various factors including the reaction temperature and the drying temperature might be altered to meet these purposes (20). With increase of the reaction temperature, the total PCB formation increases independent of reaction time after the initial 2 h (25). Lower chlorinated benzenes might produce more PCB congeners than higher ones.

During the process of perchlorination from phthalocyanine blue to phthalocyanine green, decachlorobiphenyl (PCB 209) is formed along with some other highly chlorinated

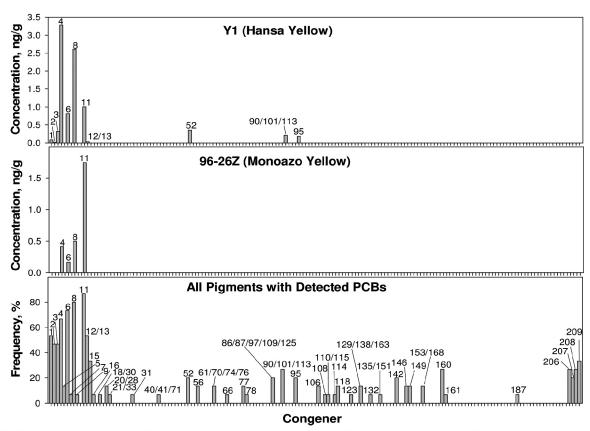


FIGURE 2. Examples of PCB profiles in paint pigments (top two plots) and the frequency of congener detection in the 15 pigments with detected PCBs (bottom plot).

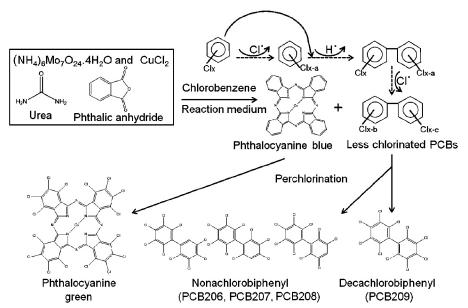


FIGURE 3. PCB formation mechanisms in the manufacture process of phthalocyanine blue and phthalocyanine green. The subscripts x, a, b, and c refer to the number of chlorine atoms.

congeners such as nonachlorobiphenyls (PCBs 206, 207, and 208) from less chlorinated congeners (Figure 3). This explains the presence of much more nona- and deca-PCB congeners in phthalocyanine green than in phthalocyanine blue, which can be observed by comparison of PCB distribution profiles in L1 and G2 from Sherwin Williams, 96-5E and 96-4D from PPG Pittsburgh, and CC and PP from Vogel.

**Azo Pigments.** Azo pigments are the most important group of synthetic colorants with the largest fraction (more than

50%) of organic pigments on the market (29). Azo pigments have a wide range of colors covering almost the entire visible spectrum although blue and green colors are mostly provided by phthalocyanine and two other pigments (18). Some vivid colors of azo pigments are commercially dominant, especially reds, oranges, and yellows.

Azo pigments are almost exclusively produced through a reaction sequence of diazotization and coupling to afford the azo group (—N=N—) which is the chromophore respon-

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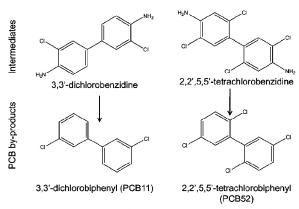


FIGURE 4. Possible formation pathways of PCB11 and PCB52 in pigments.

sible for its vivid colors (18). The reaction involves a primary aromatic amine as a diazo component and a nucleophilic aromatic or aliphatic compound with active methylene groups as a coupling component. An aromatic amine such as a mono-, di, or trichlorinated aniline is typically involved in the diazotization reaction as a diazo component, and frequently they are also used as coupling components. Another important group of diazo components for azo pigment formation include 3,3'-dichlorobenzidine, and to a lesser extent 2,2'5,5'-tetrachlorobenzidine, 3,3'-dimethoxybenzidine, and 3,3'-dimethylbenzidine (18). The last two compounds do not contain chlorines which are required elements for formation of PCB congeners.

For synthesis of azo pigments, there are more than 10 common intermediates and starting materials such as chlorinated aniline and chlorinated benzidines that can potentially have side-reactions to produce PCBs. PCBs are probably formed by coupling of bis-diazotized dichlorobenzidines or tetrachlorobenzidines under basic conditions as a result of the decomposition of the diazo moiety. Polychlorinated anilines can be also used to form PCBs through the free radical mechanism, and the free radical rearrangement of chlorine positions might play a significant role in varieties of PCB congeners with limited chlorinated intermediates. Lower PCB congeners may be formed by carrying out the coupling process at lower pH or in the presence of unsaturated aliphatic compounds such as acylamides (20). For example, 3,3'-dichlorobenzidine and 2,2',5,5'-tetrachlorobenzidine are probably the diazo components for TT and HH pigments that contain high PCB11 and PCB52 (Table S3), respectively. Unfortunately, we cannot verify the pathways for pigments considered proprietary by manufacturers; however, the links of intermediates and PCB by-products can be illustrated structurally (Figure 4). The azo pigments based on 3,3'-dichlorobenzidine appear preponderant (30), which might explain partially the consistency of PCB11 detection.

**Environmental Emission.** A wide variety of organic pigments are commercially available; however, in terms of chemical structure, almost all currently produced organic pigments belong to four different groups: azo pigments and lakes (salt type), phthalocyanine pigments, polycyclic pigments, and heterocyclic pigments (20). In spite of accelerated progress in the synthesis of organic pigments, commercially available pigments at present are chemically identical to those produced historically since the use of synthetic pigments. PCB congeners are primarily detected in azo pigments and phthalocyanine pigments. PCB11 is consistently detected in almost all azo and phthalocyanine pigments, and it is absent or in very low relative concentrations in commercial Aroclor mixtures. Therefore, PCB11 can be regarded as a key indicator of PCB emission from de novo synthesis as by-products of

industrial synthetic process of paint pigments. PCB11 is the fifth highest congener and ubiquitous in Chicago air (4). Although we do not know the contribution of PCB congeners from paint pigments to the airborne PCBs in the environment, these congeners, especially low chlorinated congeners, might contribute a significant portion as PCB11 because of their high volatility.

Based on 40 CFR 761.80, PCBs are allowed at less than 25 mg/kg with a 50 mg/kg maximum in commerce of diarylide pigments or phthalocyanine pigments when leaving a manufacturing site or imported to the United States. PCB levels in the examined paint pigments are all below the regulatory standard; however, paints are being extensively and constantly used especially in urban areas. PCBs might accumulate due to their resistance to degradation in the environment. It has been reported that PCB11 and total PCB levels in air are directly proportional to human population density (7, 31, 32). To our knowledge, pigments or dyes are the only significant source of PCB11. The elevation of PCB11 in air must be associated with human activity utilizing pigments or dyes. The presence of PCB11 indicates paint should be an important source of airborne PCBs although the link of PCBs in paint pigments and PCBs in air is still not clear.

#### Acknowledgments

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#### Supporting Information Available

Three tables. This information is available free of charge via the Internet at http://pubs.acs.org.

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